

Catalytic flameless combustion of methane over perovskites prepared by flame–hydrolysis

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Received 28 January 2001; received in revised form 2 May 2001; accepted 6 May 2001

Abstract

A set of perovskite-type catalysts of general formula $\text{LaBO}_{3\pm\delta}$ ($\text{B} = \text{Co}, \text{Mn}, \text{Fe}$) and a sample of $\text{La}_2\text{NiO}_{4\pm\delta}$ were prepared by means of a recently proposed innovative flame–hydrolysis procedure. The catalysts were characterised by nanometer-size particles (20–60 nm), relatively high surface area (ca. $20 \text{ m}^2/\text{g}$), high thermal stability and high phase purity. Their high activity for the catalytic flameless combustion of methane confirmed the validity and versatility of the preparation method.

Temperature-programmed -desorption and -reaction, coupled with mass spectrometric analysis, allowed to better understand some aspects of the catalytic behaviour shown by the present samples for the cited reaction. In particular, an interesting correlation between the availability of oxygen at various temperatures, as revealed by the so-called α and β oxygen desorption peaks, and reaction mechanism was found for the different B metals. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Perovskite-like catalysts; Flame–hydrolysis preparation; Methane catalytic flameless combustion mechanism

1. Introduction

The abatement of pollutants such as CO , NO_x and unburned hydrocarbons in combustion exhausts is gaining ever growing attention. In particular, it is well-known that catalytic flameless combustion (CFC) of hydrocarbons limits or virtually suppresses the formation of these harmful compounds, being carried out at considerably lower temperature (below 800°C) with respect to usual combustion. So far, the catalysts employed for CFC reactions are based on supported noble metals. However, besides being expensive, the latter easily sinterise and can form harmful volatile compounds. Among the possible substitutes for noble metals, perovskite-type transition metal mixtures,

if prepared in the appropriate way, showed comparatively active, highly resistant to deactivation and much cheaper.

Perovskites are mixed oxides of general formula $\text{ABO}_{3\pm\delta}$, where A is usually a lanthanide ion and B is a transition metal ion. Both A and B can be partially substituted, leading to a wide variety of compounds of general formula $\text{A}_{1-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_{3\pm\delta}$, characterised by structural and electronic defects, owing to their non-stoichiometry. For the complete oxidation reactions, such as the CFC, the metal B ion is considered the responsible of catalytic activity [1], while the cation A, especially when partially substituted with an ion A' of different valence, determines the formation of crystal lattice vacancies and can stabilise unusual oxidation states for B, leading to different catalytic performance [1–3]. The activity of perovskites has been ascribed to their ionic conductivity, to oxygen mobility within the lattice [2], to their reducibility and

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to oxygen sorption property [4]. The mobility of O^{2-} ions determines the mechanism of the oxidation reaction. Indeed, two possible mechanisms, a suprafacial and an intrafacial one, were proposed since long time [5] and now accepted. The former mechanism, active at lower temperature ($T < 400^\circ\text{C}$), is due to surface oxygen; the latter, active at $T > 400^\circ\text{C}$, is connected with the intervention of bulk oxygen, continuously replaced by the gaseous oxygen through a Mars–Van Krevelen mechanism.

Temperature-programmed desorption (TPD) of oxygen showed a powerful technique for the evaluation of catalyst affinity towards oxygen [2,3]. During the TPD analysis of pre-adsorbed oxygen, two desorption peaks, called α and β , can be observed, relative to the release of oxygen, adsorbed on the surface or migrating from the bulk, respectively [3,6–9].

The preparation procedure determines the properties of the catalysts obtained. The traditional calcination–milling (CM) route for preparing such materials ends in a low surface area, less active catalyst. Hence, several techniques were developed [3,10], in order to overcome this problem, the most commonly used being the so-called sol–gel–citrate (SGC) method. This leads to catalysts of high surface area (up to $50\text{ m}^2/\text{g}$), so highly active, which, however, rapidly sinterise under the usual CFC conditions, due to the too low temperature ($<800^\circ\text{C}$) attained during preparation.

In some previous papers [3,10], we presented a new method for the preparation of perovskitic mixed oxides, through flame–hydrolysis (FH) of an aqueous solution of the precursor salts. A series of high surface area catalysts were obtained, active for the CFC of methane. The aim of the present work was to check the versatility of the method, by preparing a set of perovskites of general formula $\text{LaBO}_{3\pm\delta}$ ($B = \text{Co}$, Mn , Fe) or $\text{La}_2\text{BO}_{4\pm\delta}$ ($B = \text{Ni}$). These catalysts have been characterised by N_2 adsorption–desorption, X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray fluorescence (XRF). Temperature-programmed desorption–mass spectrometry (TPD–MS) of pre-adsorbed oxygen or methane were employed in order to deepen some aspects of catalyst activity and of methane CFC mechanism. The catalytic activity was tested both by means of a fixed bed, continuous microreactor and through different Temperature-programmed reaction–mass spectrometry (TPR–MS) experiments.

2. Experimental

2.1. Catalyst preparation

A detailed description of our new FH procedure for catalyst preparation can be found elsewhere [10]. Briefly, the precursor salts (La , Co , Ni , Mn , Fe acetates or nitrates), in the desired ratios, were dissolved in water, or, when necessary, in 10% HNO_3 . Citric acid was then added as a complexing agent, in 0.5/1 molar ratio with respect to the sum of metal salts. The clear solution obtained was nebulised by means of a small nozzle into an oxy–hydrogen flame. The estimated temperature of perovskite formation was 1600 – 1800°C and the residence time of the reagents in the hottest zone of the flame was a very few milliseconds. The nanometric-size particles so obtained were collected by means of a 10 kV electrostatic precipitator.

2.2. Catalyst characterisation

BET surface area and porosity of every sample were determined by means of a Micromeritics ASAP 2010 instrument. XRD analysis was carried out by means of a Philips PW1820 powder diffractometer, by using the Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418\text{ nm}$). Solid phases were identified by comparison of diffractograms with literature data [11]. Morphology and particle size was determined by means of a Cambridge Stereoscan 150 Scanning Electron Microscope. The composition of every sample was determined by XRF, by means of a Jordan–Valley model EX310 instrument, calibrated by analysing oxide mixtures of known composition.

2.3. Catalytic activity tests

The bench-scale continuous apparatus for testing activity for CFC of methane was centred on a down-flow quartz reactor, 7 mm i.d., fitted with a 1.6 mm o.d. axial thermowell. The reactor was heated by an electric furnace, controlled by an Eurotherm, model 812, TRC. An amount of 0.2 g of catalyst, pressed into wafers, then ground and sieved to 0.15–0.25 mm particles, were loaded in the isothermal middle part of the reactor, after dilution with 1.3 g of quartz of the same particle size. The void space over and below the catalyst bed was filled with quartz beads (0.25–0.85 mm).

The catalyst was activated by flowing 20 cm³/min of air, while increasing temperature (10°C/min) up to 600°C, then kept for 1 h. After cooling in flowing air down to 250°C, the activity tests were carried out by feeding 10 cm³/min of a mixture of CH₄ (1.04 vol.% in He) together with 10 cm³/min of air, while increasing temperature (2°C/min) from 250 up to 600°C. The gas flow rates were regulated by means of MKS mass flow-meters (model 1259 CC), governed by a MKS model 247C control unit. The outlet gas was analysed by means of a HP model 5890A HWD gas chromatograph, equipped with Porapak Q and MS 5A columns.

2.4. TPD–TPR–MS analysis

A detailed description of the TPD–TPR–MS apparatus was given in a previous paper [12]. The catalyst (0.8 g, 0.15–0.25 mm particle size) was loaded in a quartz reactor, heated by an electric furnace controlled by an Eurotherm, model 822, TRC. Prior to every TPD or TPR run the catalyst was heated (10°C/min) up to 800°C in flowing He (purity ≥ 99.9999 vol.%).

TPD of pre-adsorbed oxygen was carried out in He as carrier gas (20 cm³/min), after an overnight saturation of the sample in 20 cm³/min of air (purity ≥ 99.9995 vol.%) at 750°C, followed by cooling down to 50°C. The following temperature programme was adopted: the catalyst was kept at 50°C for 10 min, the temperature was then raised (10°C/min) to 800°C, then kept for 10 min. The composition of the outlet gas was monitored by means of a quadrupolar mass spectrometer (QMS), MKS model PPT Residual Gas Analyser.

A further TPD experiment was carried out in order to check the possible activation of the substrate. Methane pre-adsorption was carried out by keeping the catalyst for 4 h at 250°C in a stream of CH₄ (1.04 vol.% in He) and cooling slowly down to 50°C. The TPD test was then carried out as described.

Three different TPR–MS experiments were performed, through either continuous or pulsed method. The sample was saturated in air as described, then the previously mentioned gas mixture (10 cm³/min of CH₄ 1.04 vol.% in He and 10 cm³/min of air) was fed to the reactor. This mixture was either fed continuously (first experiment), or injected as 1.2 cm³ pulses (second experiment) into the He carrier gas, before the reactor, while running the temperature programme

previously reported for the TPD experiment. The third experiment was done by feeding continuously 20 cm³/min of 1.04 vol.% CH₄ in He gas mixture, after pre-saturation of the sample in air. The MS species monitored were CH₄ ($m/z = 15$, in order to avoid confusion with the $m/z = 16$ fragment of O₂), H₂O ($m/z = 18$), N₂ ($m/z = 14$, to distinguish it from CO), O₂ ($m/z = 32$), CO₂ ($m/z = 44$), CO ($m/z = 28$) and NO ($m/z = 30$).

3. Results and discussion

The practical application of the present FH method for the preparation of perovskitic mixed oxides requires the checking of its possible limits and versatility. In our previous papers [3,10], we described the preparation and characterisation of a series of La cobaltates, partially substituted with Ce or Eu for La at various substitution degrees, which perfectly matched our requests of high surface area, high activity for the CFC of methane and high thermal stability. In order to check the versatility of the preparation procedure, in the present work we have prepared a series of non-substituted lanthanum perovskites, characterised by different B metals (LaBO_{3±δ}). Indeed, there are some important parameters to be adjusted during preparation, as already pointed out [10], such as the nature of the precursor salts, the concentration of the solution to be nebulised, the nature of the complexing agent, the feeding rate of precursors solution and the flame temperature. Changing the B metal implies, e.g. the availability of a precursor salt, soluble in water or in diluted nitric acid and able to lead to a perfectly clear and stable feeding solution of the desired composition and concentration. Particularly, the latter determines productivity, surface area and crystallinity of the prepared perovskite.

3.1. Catalyst characterisation

The XRD analysis (Fig. 1) confirmed the presence of a perfectly pure and crystalline perovskitic phase for LaFeO_{3±δ} and LaCoO_{3±δ}. The diffractogram obtained for LaMnO_{3±δ} shows two additional weak peaks at $2\theta = 26$ and 46° , probably because of the tendency of Mn to remain stable in a higher number of different oxidation states, with respect to Fe and

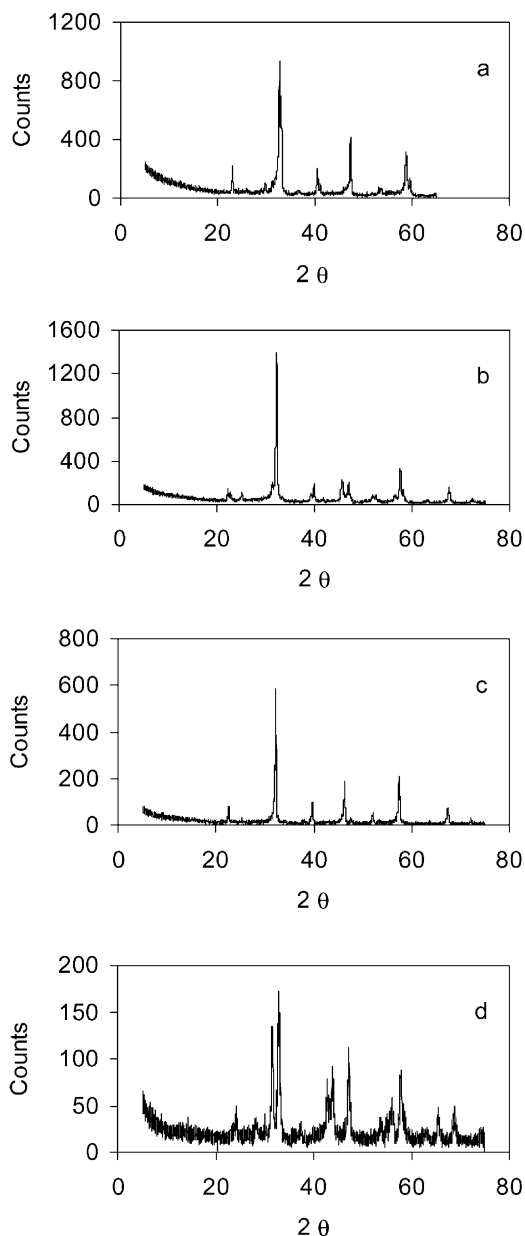


Fig. 1. X-ray diffractograms relative to $\text{LaCoO}_{3\pm\delta}$ (a); $\text{LaMnO}_{3\pm\delta}$ (b); $\text{LaFeO}_{3\pm\delta}$ (c); and $\text{La}_2\text{NiO}_{4\pm\delta}$ (d).

Co. This leads to different possible ion coordination within the lattice, leading to the formation of some additional spurious phase(s). As for Ni, the only phase forming under the present preparation conditions was $\text{La}_2\text{NiO}_{4\pm\delta}$. This oxide has a tetragonal structure [11]

and belongs to a well-known family of perovskite homologues with general formula $\text{A}_2\text{BO}_{4\pm\delta}$. They possess a compact structure, including a perovskitic layer (general formula ABO_3), intergrown with a layer with “rock salt” arrangement (general formula AO). This confirms that the insertion of Ni in the ABO_3 perovskitic lattice is more difficult, being the Ni^{2+} oxidation state very stable.

The BET surface area (S_{BET}) of the present catalysts was measured on fresh and on aged (i.e. after use as catalysts for the CFC of methane) samples. No significant change of S_{BET} was noticed after ageing, the value for fresh and aged sample matching to each other, within the experimental error ($\pm 4\%$). S_{BET} values ranged from $22.8 \text{ m}^2/\text{g}$ for $\text{La}_2\text{NiO}_{4\pm\delta}$ to $15.6 \text{ m}^2/\text{g}$ for $\text{LaFeO}_{3\pm\delta}$. These values fall between those obtained through the traditional SGC and CM preparation procedures, but they can be considered quite high, when taking into account the very high calcination temperature (over 1600°C) reached during the FH. The compromise between high surface area and high calcination temperature is made possible by the formation of nano-particles. Indeed, SEM analysis showed that the present catalysts are constituted of 20–60 nm spheroidal particles, usually conglomerated into 100–500 nm clusters. By decreasing the diameter of the nozzle used to nebulise the precursor solution, a further decrease of the particle size can be obtained [10], so increasing the surface area. However, this would be accompanied by a strong decrease of process productivity. Hence, a compromise has to be reached between these two points.

The real composition of the present catalysts was determined through qualitative and quantitative XRF analysis. Qualitative analysis excluded the presence of any extraneous element. Quantitative analysis confirmed, within the experimental error ($\pm 1 \text{ wt.}\%$), a good correspondence between the real composition and the nominal one, calculated from the weighted amounts of precursor salts.

3.2. Catalytic activity

The results of the activity tests are collected in Fig. 2. In Table 1, the values of T_b , $T_{1/2}$ and T_c , representing the temperature of light-off, of half-transformation and of complete conversion of methane, respectively, are reported. For the samples showing a

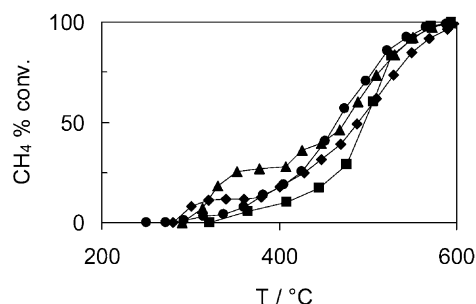


Fig. 2. CH₄ conversion vs. temperature for the various catalysts: (●) LaCoO_{3±δ}; (◆) LaMnO_{3±δ}; (▲) LaFeO_{3±δ}; (■) La₂NiO_{4±δ}.

low-temperature partial conversion, a further value of T_b is reported, indicated by T_b^* . The catalyst showing the lowest value of T_b^* was LaMnO_{3±δ}, followed by LaFeO_{3±δ} and LaCoO_{3±δ}. The Ni-based sample showed the lowest value of T_c . Every sample allowed 100% methane conversion to be reached around 600°C (Fig. 2). However, the strongest differences between these catalysts can be observed by considering $T_{1/2}$. Indeed, the lowest value of $T_{1/2}$ was observed with LaCoO_{3±δ}, as expected, being this catalyst one of the most active for the CFC of hydrocarbons, while La₂NiO_{4±δ} showed the highest value of $T_{1/2}$.

Another important difference may be observed as for the reaction mechanism. LaMnO_{3±δ}, LaFeO_{3±δ} and, to a lower extent, LaCoO_{3±δ}, showed some more or less important low-temperature conversion. By contrast, La₂NiO_{4±δ} showed a much lower conversion between 320 and 500°C. The activity of this set of samples did not seem to be connected with their surface area, which, indeed, was rather similar. It can be better explained by considering the different behaviour of the B metal ion into the oxide lattice. Indeed, it is well-known [1] that unsubstituted ABO₃

perovskites usually are active through the suprafacial mechanism. The reason has to be searched in the ionic mobility within the lattice. When oxygen mobility is low, the suprafacial mechanism is usually active, while a high ionic mobility favours the participation of bulk oxygen, so that the intrafacial mechanism is preferred. Hence, one may conclude that oxygen mobility is higher for La₂NiO_{4±δ} and LaCoO_{3±δ} than for LaMnO_{3±δ} and LaFeO_{3±δ}. The Fe-based sample, indeed, showed the highest suprafacial activity within this series, attaining almost 30% methane conversion at low temperature.

3.3. TPD–MS analysis

If catalytic activity for the complete oxidation reaction on perovskites is connected with oxygen mobility, then TPD analysis of pre-adsorbed oxygen can be a powerful method for the characterisation of these materials. It is well-known [9] that, when a perovskite is heated in inert atmosphere at high temperature, usually around 800°C, oxygen vacancies can form. By cooling in air, these vacancies are filled with adsorbed oxygen and the charge compensation is provided by partial oxidation of the metal B ion. A TPD analysis after this pre-treatment reveals two possible desorption peaks, called α and β , widely reported in literature [1,3,7–9]. The α peak, usually observed at lower temperature, represents the desorption of oxygen adsorbed on the catalyst surface and it is not always observable, depending on the concentration of filled oxygen vacancies. In particular, its onset temperature and intensity depend partially on the nature of metal B, but mainly on the substitution degree of the A ion with a cation of different valence [3,7]. The β peak, characterised by higher onset

Table 1

Temperature of light-off of the suprafacial (T_b^*) and intrafacial (T_b) reaction mechanisms, of methane half-transformation ($T_{1/2}$) and of methane complete conversion (T_c), of the catalysts prepared, as determined by either activity tests or continuous TPR–MS experiments^a

Catalyst	Activity tests				TPR–MS		
	T_b^*	T_b	$T_{1/2}$	T_c	T_b	$T_{1/2}$	T_c
LaCoO _{3±δ}	(>290)	380	466	602	(375)	503	630
LaMnO _{3±δ}	270	380	489	605	278	500	648
LaFeO _{3±δ}	290	400	472	596	290	476	592
La ₂ NiO _{4±δ}	–	320	497	594	330	480	601

^a Data in parentheses indicate less accurate determination.

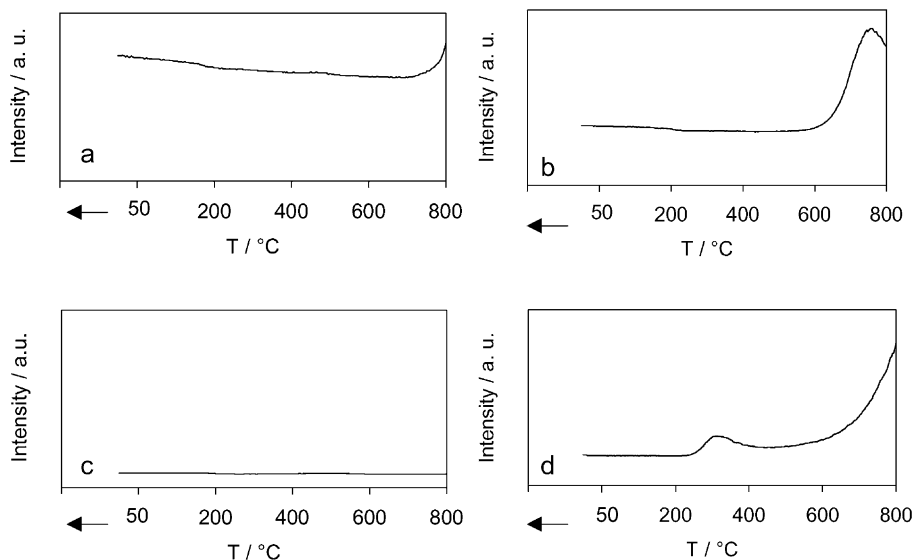


Fig. 3. Oxygen TPD-MS patterns ($m/z = 32$ signal) for the various catalysts: (a) $\text{LaCoO}_{3\pm\delta}$; (b) $\text{LaMnO}_{3\pm\delta}$; (c) $\text{LaFeO}_{3\pm\delta}$; and (d) $\text{La}_2\text{NiO}_{4\pm\delta}$.

temperature, strictly depends on the nature of the B ion, being correlated to its partial reduction to a lower oxidation state [7,9]. The onset temperature of the β peak is usually very near to that of thermal decomposition of the pure B metal oxide. For instance, the decomposition temperature of pure Co_2O_3 (895°C) is very near to the onset temperature of the $\text{LaCoO}_{3\pm\delta}$ β peak [3] and a similar consideration can be extended also to Mn- and Ni-containing perovskites [8].

The set of catalysts here prepared showed different TPD patterns, depending on the nature of B ion. Indeed, $\text{La}_2\text{NiO}_{4\pm\delta}$ showed a relatively intense α peak around 300°C (Fig. 3), while the onset temperature of the β peak was approximately 650°C . Furthermore, the maximum of the β desorption peak was not reached within the upper temperature limit (800°C) of our apparatus. $\text{LaMnO}_{3\pm\delta}$ did not show any α desorption peak, while the onset temperature of the β peak was perceptibly lower than in the previous case, leading to a lower and broader maximum of the β desorption peak at 700 – 750°C . $\text{LaCoO}_{3\pm\delta}$ showed a very small, almost undetectable α peak around 450°C and a β peak, starting over 700°C . Finally, $\text{LaFeO}_{3\pm\delta}$ showed neither α nor β peak within the temperature range investigated.

The appearance of an intense α peak is due to a high concentration of oxygen vacancies. Hence, one may conclude that $\text{La}_2\text{NiO}_{4\pm\delta}$ is highly defective from this point of view, $\text{LaCoO}_{3\pm\delta}$ possesses a lower concentration of vacancies, while $\text{LaMnO}_{3\pm\delta}$ and $\text{LaFeO}_{3\pm\delta}$ do not possess this kind of defects quite at all.

By partially substituting the metal A ion, it is possible to introduce different defective sites, such as anionic vacancies, and/or to stabilise unusual oxidation states for the metal B ion. As already reported for a series of partially substituted lanthanum cobaltates [3], the increase of oxygen vacancies can be confirmed through TPD analysis. Indeed, the substitution of Ce or Eu for La leads to a change of the intensity and of the onset temperature of the α peak. The present results, in addition, show that the α peak is not due to the A substitution only, but it is tied also to the nature of the B metal.

The presence of the β peak and its onset temperature can be adopted as a qualitative description of catalyst reducibility and oxygen mobility within the oxide. Both these parameters are fundamental to describe catalytic activity. Indeed, according to the intrafacial mechanism proposed by Voorhoeve et al. [5], a redox cycle involving metal B is responsible of the substrate oxidation and of the regeneration of the metal, back

to the original valence, by the gaseous O_2 present in the reaction atmosphere. An easy reducibility of the B metal, i.e. a low-temperature β peak, would make easier this step. Moreover, a quick oxygen transport through the perovskitic lattice would be favourable for the same reasons. Oxygen mobility is tightly connected with the presence and concentration of oxygen vacancies: the higher their concentration, the lower is the activation energy for oxygen transport. Almost no oxygen mobility was observed with non-substituted stoichiometric lanthanum perovskites [2], while ionic conductivity increased with La substitution. However, the conductivity seems to be connected also with the nature of B metal. Indeed, the activation energy for oxygen transport is reported to be higher for Mn than for Co substituted perovskites [2].

The present results allow us to interpret the catalytic activity tests. Indeed, the presence of a suprafacial or of an intrafacial mechanism is tightly connected with oxygen mobility and, therefore, with the amount of oxygen vacancies. Hence, the catalysts that did not show any α peak, i.e. that are not characterised by oxygen vacancies, revealed very active at low temperature through the suprafacial mechanism. This confirms the previously hypothesised low oxygen mobility in $LaFeO_{3\pm\delta}$ and $LaMnO_{3\pm\delta}$. By contrast, the catalysts characterised by the presence of a more or less intense α peak, such as $La_2NiO_{4\pm\delta}$ and, to a minor extent, $LaCoO_{3\pm\delta}$, showed to be exclusively or predominantly active through the intrafacial mechanism.

In addition to these O_2 TPD experiments, we performed also a TPD analysis after pre-adsorption of methane. No desorption signal was observed, indicating that methane does not adsorb in detectable amount and, hence, that catalytic activity is due to oxygen mobility, rather than to the direct activation of the substrate to be oxidised.

3.4. TPR–MS analysis

The results of the pulsed and continuous TPR–MS tests, carried out by feeding the mixture of CH_4 (1.04% in He) and air, matched almost perfectly for every sample. However, the values of T_b , $T_{1/2}$ and T_c , reported in Table 1, have been determined from the continuous experiments, due to a more precise estimation. Both the suprafacial and the intrafacial

reaction mechanisms have been observed also through these experiments, though less clearly. Furthermore, the TPR–MS results matched quite precisely those of the activity tests, confirming $LaMnO_{3\pm\delta}$ as the catalyst showing the lowest T_b and the highest T_f value. The higher value of T_b obtained for $LaCoO_{3\pm\delta}$ (see Table 1) was due to the small intrafacial reaction contribution, difficult to detect in these qualitative experiments. Indeed, when the low-temperature methane conversion is very low, it is difficult to determine precisely the light-off temperature of the reaction.

In addition, some TPR–MS reaction/regeneration cycles, carried out on the same catalyst sample, showed no change in catalytic activity nor in catalyst properties, so confirming the high thermal stability of the perovskites prepared by the FH procedure.

The TPR–MS experiments, carried out by feeding only CH_4 after O_2 pre-adsorption, allowed us to determine the possible influence of the different (α and β) oxygen species on catalytic activity. The Ni-containing sample began to be active at $400^\circ C$ and conversion attained 100% at $750^\circ C$. The α peak was still observable, while the β one completely vanished. The same shift of the light-off temperature was observed with $LaMnO_{3\pm\delta}$, though the shift of the final temperature was less pronounced. It has to be noticed that in this last case a weak β peak became observable only after complete methane conversion. A similar behaviour was observed for $LaCoO_{3\pm\delta}$. On the other hand, a different pattern was obtained for $LaFeO_{3\pm\delta}$. Indeed, methane conversion was still incomplete even at $800^\circ C$ and CH_4 consumption rate was slower than for the other samples.

It may be concluded that bulk oxygen only was involved in the reaction, the species adsorbed on the surface seeming unaffected. Very likely, α desorption takes place at a too low temperature to be useful for the reaction. Indeed, when the TPR experiment was carried out by feeding CH_4 + air, the surface sites set free after α desorption could be filled by new oxygen species coming from the reaction atmosphere and readily activated. So, when the onset temperature for the reaction was reached, activated oxygen was available. By contrast, when oxygen was absent in the reaction atmosphere, the light-off temperature was shifted towards higher values, i.e. towards the onset temperature of oxygen β desorption. Such oxygen

species are those available at the right temperature for the reaction. This is confirmed by the β desorption onset temperature of the Ni- and Mn-containing samples, which was shifted up to after complete methane conversion.

4. Conclusions

In the present work, the high versatility of our FH preparation method has been confirmed. All the present samples were characterised by high crystallinity, high surface area and high activity for the CFC of methane, as well as by high thermal resistance.

For Fe-, Mn- and, to a much lower extent, for Co-based perovskites, the suprafacial, low-temperature activity was observed, due to a low oxygen mobility within their crystal lattice. This was confirmed by the absence of any strong oxygen α desorption peak during the TPD experiments. $\text{La}_2\text{NiO}_{4\pm\delta}$ showed the opposite behaviour.

The TPR–MS experiments confirmed the activity data. In particular, those carried out by feeding CH_4 after O_2 pre-adsorption revealed that α desorption does not affect catalyst activity, mainly because it takes place at a temperature lower than that of reaction light-off. While in the presence of O_2 in the reaction atmosphere the vacancies can be readily filled, leading to oxygen activation, in its absence it is necessary to wait for the β desorption onset to observe a high catalytic activity.

Acknowledgements

The valuable help of L. Fabbrini in preparation of catalysts and the financial aid of the Italian National Council for Research (CNR) through the PF-MSTA-II, Contract no. 99.01789.PF 34, are gratefully acknowledged.

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